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**CATALYTIC MULTI-STAGE LIQUEFACTION OF COAL
TWELFTH QUARTERLY REPORT FOR THE PERIOD**

1 JULY 1995 - 30 SEPTEMBER 1995

A.G. Comolli
E.S. Johanson
L.K. Lee
V.R. Pradhan
R.H. Stalzer

FINAL

WORK PERFORMED UNDER CONTRACT

DE-AC22-93PC92147

**HYDROCARBON TECHNOLOGIES, INC.
PO BOX 6047, NEW YORK & PURITAN AVENUES
LAWRENCEVILLE, NJ 08648**

DECEMBER 1995

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TABLE OF CONTENTS

Abstract	1
Summary	2
Task 2 - Laboratory Scale Studies	3
Task 3 - Bench-Scale Studies	4
Run CMSL-11 (227-89): Evaluation Of A Combined Iron-Molybdenum Dispersed Slurry Catalyst System for Direct Liquefaction of Black Thunder Mine Coal and its Coprocessing with Waste Plastics	4
Summary	4
Background, Objective, And Scope Of Work	5
Operational Details	8
Process Performance	8
Product Quality	10
External Samples	11
Conclusions	12
Recommendations For Future Work	13
Task 4- Technical Assessment	14
Task 5- Project Management	15

LIST OF TABLES

Table 1 -	Laboratory Support for CMSL-11 Run: Analysis of Waste Plastics	3
Table 2 -	CMSL-11: Intended Run Plan	16
Table 3 -	CMSL-11: Actual Run Plan	17
Table 4 -	CMSL-11: Process Performance Summary	18
Table 5 -	Dispersed Catalyst Performance During CMSL-09, 10, and 11	19
Table 6 -	CMSL-11: Separator Overhead (SOH) Inspection	20
Table 7 -	CMSL-11: Properties Of Pressure Filter Liquids (Stage II)	21
Table 8 -	CMSL-11: Inspection Of Pressure Filter Solids (Stage II)	22
Table 9 -	CMSL-11: List Of External Process Samples	23
Table 10 -	CMSL 09: Summary of Economics	24
Table 11 -	CMSL 10: Summary of Economics	25
Table 12 -	CMSL 11: Summary of Economics	26

LIST OF FIGURES

Figure 1 -	CMSL 11: Daily Material Balance	27
Figure 2 -	CMSL 11: Daily Feed Space Velocities	28
Figure 3 -	CMSL 11: Daily Reactor Temperatures	29
Figure 4 -	CMSL 11: Feed Composition	30
Figure 5-	CMSL 11: Conditions vs. Catalyst Concentrations	31
Figure 6 -	CMSL 11: Relative Thermal Severity	32
Figure 7 -	CMSL 11: Feed And Resid Conversions	33
Figure 8 -	CMSL 11: C4-524°C Distillate Yields	34
Figure 9 -	CMSL 11: Distillate Selectivity	35
Figure 10 -	CMSL 11: Gas Yields and H ₂ -Consumption	36
Figure 11 -	CMSL 11: PFL Solubility	37
Figure 12-	CMSL-09: Economic Effects of Plastics on Cost	38
Figure 13-	CMSL-09: Economic Effects of Iron Catalyst Rate	39

ABSTRACT

This quarterly report covers the activities of Catalytic Multi-Stage Liquefaction of Coal during the Period July 1 - September 30, 1995, at Hydrocarbon Technologies, Inc. in Lawrenceville, New Jersey. This DOE Contract Period was from December 8, 1992 to December 7, 1994 and has been extended to September 30, 1995.

The overall objective of this program is to produce liquid fuels from coal by direct liquefaction at a cost that is competitive with conventional fuels. Specifically, this continuous bench-scale program contains provisions to examine new ideas in areas such as: low temperature pretreatments, more effective catalysts, on-line hydrotreating, new coal feedstocks, other hydrogen sources, more concentrated coal feeds and other highly responsive process improvements while assessing the design and economics of the bench-scale results.

This quarterly report covers work on Laboratory Scale Studies, Continuous Bench-Scale Operations, Technical Assessment and Project Management.

SUMMARY

This report describes the following: i) Laboratory scale studies in support of CMSL-11, ii) Bench Run CMSL-11, and iii) Technical Assessment on Bench Runs CMSL-09, 10, and 11.

The laboratory scale studies consisted of assessing the dissolution/mixing behavior of the “real life” municipal solid waste plastics (obtained from the Monmouth Recycling, NJ) in coal-derived oils. An effort was also made to estimate the elemental composition and other analytical properties of this waste plastics. The Bench Run CMSL-11 was conducted over a period of 17 days of operation spanning over four operating conditions. The effects of dispersed catalysts, based on iron and molybdenum, were studied on direct liquefaction of coal and also coal/waste plastics coprocessing. Both iron and molybdenum (at 5000 and 100 ppm respectively), in tandem, were found effective for obtaining high conversions and yields. It was found that the addition of iron and molybdenum from individual precursors was more effective than using a bimetallic iron-molybdenum catalyst precursor. The coal and resid conversions of about 95 and 90 Wt% maf were obtained during ‘coal-only’ conditions. High light gas yields (15-18 Wt% maf) were also obtained. These went down during the ‘coal-plastics’ coprocessing conditions. The overall light distillate yields also went up by as much as 3-5 Wt% maf during coprocessing conditions (while the chemical hydrogen consumption dropped by 40 %). This increase in the light distillate yields during CMSL-11 was not as substantial as observed during the earlier runs, CMSL-08 and CMSL-09. This was probably because the “real life” MSW plastics employed during CMSL-11 was found to contain over 90 Wt% high density polyethylene, HDPE, the hardest of the plastics to convert to light liquids and gases.

Technical assessment and economic analysis has been performed on the last three CMSL-runs in this contract during the reporting period. These three CMSL runs investigated liquefaction in an all-dispersed-catalyst system, with coal and coal/plastics mixtures. The coal in each run was sub-bituminous and the plastics were mixtures of polyethylene, polystyrene and polypropylene. The plastics content of the total liquefaction feed varied from zero to fifty percent. The dispersed catalyst was a mixture of Molyvan A and Iron.

TASK 2 - LABORATORY SCALE STUDIES

In order to assess the dissolution/mixing behavior of the “real life” mixed plastics in coal-derived oil, 50 parts of an L-814 oil were preheated to 200°C with constant agitation. The pieces of shredded plastics (manually cut) were added over a span of 15 minutes to the hot oil to achieve a mixture that was 50% plastics. The mixture was stirred hot for an additional 30 minutes while increasing the temperature to 225°C. The mixture was found to be homogeneous and without any apparent lumps. It was viscous, as expected. This 50/50 w/w homogeneous mixture of waste plastics and L-814 oil was cooled, and elemental and other analyses were performed on pure L-814 oil and the plastic-oil mixture. The properties of the waste plastics was thus estimated by difference. These analyses are listed in Table 1.

TABLE 1. Laboratory Support for CMSL-11: Analyses of Waste Plastics

Property	50/50 Mixture of oil-plastics	L-814 oil	Waste Plastics*
Elementals, W%			
C	84.55	88.59	80.51
H	9.98	8.54	11.42
N	0.03	0.11	0.00
S	1.05	1.89	0.21
ASTM Ash, W%	0.82	0.01	1.64
Toluene Insols, W%	46.10	0.94	91.26
Cyclohexane Insols, W%	48.74	3.32	94.16

*Estimated by Difference,

TASK 3 - BENCH-SCALE STUDIES

RUN CMSL-11 (227-89)

EVALUATION OF A COMBINED IRON-MOLYBDENUM DISPERSED SLURRY CATALYST SYSTEM FOR DIRECT LIQUEFACTION OF BLACK THUNDER MINE COAL AND ITS COPROCESSING WITH WASTE PLASTICS

SUMMARY

Bench Run CMSL-11 (227-89) was carried out using a two-stage, close-coupled, back-mixed reactor system with dispersed slurry catalysts based upon iron and molybdenum. The two-stage conversion reactors were preceded by a pre-heater coil for the sulfidation of dispersed catalyst. The entire bench run, initially planned for sixteen operating days and five conditions, actually was operated for 17 days, and valuable process performance data from four operationally smooth and meaningful conditions were obtained.

During the first two run conditions, with the coal-only feed, high total coal (over 95 % maf) and 524°C+ resid conversions (89-91% maf) were obtained with 63-65% maf liquid yields. These conditions employed as little as 5000 ppm iron from HTI's proprietary catalyst and 50-100 ppm molybdenum (50 ppm from Molyvan-A and 50 ppm from HTI's Fe-Mo bimetallic catalyst). Because of the high process severities during these two conditions, very high yields of light (C₁-C₃) hydrocarbon gases (15-18 % maf) were also obtained. During Condition 2, employing 50 ppm molybdenum, from the HTI's bimetallic combination catalyst, in addition to 50 ppm from Molyvan-A, almost equivalent process performance was obtained as in Condition 1. Thus, the advantage of additional molybdenum from HTI's bimetallic catalyst was not evident from the performance during Condition 2. These two conditions presented some operational problems resulting from the high viscosities (over 2000 cps @ 300°F) of the feed slurries and difficulty encountered during solids separations by pressure filtration.

During the coal/waste plastics coprocessing conditions, an initially intended run plan had the individual color-regrinds of HDPE, high-impact polystyrene (HIPS), and polypropylene wastes feeding to the unit with coal. In reality, it was found that one of these plastics, possibly HIPS, would not completely homogenize with the recycle oil which made pumping of the highly viscous slurries impossible. Therefore, for Period 13B onwards a switch was made to a "real life" waste plastics obtained from the Monmouth, New Jersey Recycling Facility to coprocess with coal. During this coprocessing condition, both 33 wt% and 25 wt% mixed waste plastics, which were cleaned and shredded in house prior to the run, were fed together with coal. The introduction of waste plastics in the feed with coal made the recycle solvent more paraffinic and lighter as compared to the 'coal-only' conditions. As a result, pressure filtration became faster and easier. All other process conditions such as severity and catalyst concentrations, were kept the same as in 'coal-only' condition 2. Interestingly, during the coprocessing conditions, the light distillate yield increased by 3-5%; the yield of light hydrocarbon gases decreased by as much as 50% (relative) while the hydrogen consumption decreased from about 6.5% during the 'coal-only' conditions to about 3.9-4.7% (dry basis). Thus, it is now evident that even with a 'real life' MSW plastic, coprocessed with

coal, better hydrogen utilization can be obtained. The yield of heavy resid (524°C⁺) increased during the coprocessing conditions. The presence of HDPE in waste plastics contributes to the high resid (this is mostly waxy in nature) formation. In future bench experiments, it would be worthwhile to introduce fresh dispersed catalyst (more specifically molybdenum) into the higher temperature second stage conversion reactor.

The in-line hydrotreater, when it was on-line, yielded distillates with less than 50 ppm sulfur and nitrogen. The overall quality of the products from coprocessing during this was apparently different from the earlier coprocessing runs with 'simulated' waste plastic mixtures. This can be attributed to the heterogeneous nature of the actual plastic waste employed during this run. Various process stream samples, collected for Consol, Inc. for detailed analyses, should shed some light on the effect of the starting waste plastic composition on product properties.

BACKGROUND, OBJECTIVE, AND SCOPE OF WORK

The CMSL Project is geared to evaluate different novel processing concepts in catalytic coal liquefaction to complement the larger scale process demonstration "proof-of-concept" studies for the U.S. DOE. The new ideas being explored in this program include low temperature pretreatments, more effective catalysts, on-line hydrotreating, new coal feedstocks, other (cheaper) sources of hydrogen, more concentrated coal-slurry feeds, waste hydrocarbon streams, etc.

Bench Run CMSL-11 was carried out using a dispersed catalyst-only, two-stage, close-coupled back-mixed reactor system. The two-stage conversion reactors were preceded by a pre-heater coil which allowed feed slurry a residence time of about five minutes at 300°C. The pre-treatment coil was used for sulfidation of the dispersed catalyst additive. Bench run CMSL-11 was seventeen days long, comprising five operating conditions (3-5 days each). The objectives of this bench operation were:

- To determine the process performance for subbituminous coal liquefaction catalyzed by novel combinations of iron and molybdenum dispersed slurry catalysts at different process severities.
- To investigate the effect of pretreater residence time on the activity of dispersed catalyst.
- To determine the impact of using "real life" mixed waste plastics, recovered from a MSW facility, upon overall process performance in coprocessing with coal.
- To study the preconversion reactor processing/handling of the "real life" mixed waste plastics, wastes to convert such plastic waste from an as-received form to a "processed" form, suitable for feeding with coal.

An in-line hydrotreater was used during this run (except for Period 17). Both the separator (O-1) overheads, including knockouts and the ASOH, were sent through the hydrotreater as long as the atmospheric still was operating.

The initial run plan (Table 1) included five run conditions that were selected to meet the technical objectives specified above. The first two run conditions were to delineate the role of HTI's new Fe-Mo-SO₄ formulation slurry catalyst vs. individually added iron and molybdenum precursors. When added separately, HTI's Fe-SO₄ formulation precursor (employed successfully during CMSL-10) was used for iron and Molyvan-A was used as a source of Mo. During Condition 3, reactor temperatures were to be increased along with feed space velocity to maintain overall process severity; the amount of molybdenum added was to be increased from 50 to 100 ppm during this condition. The next two conditions, 4 and 5, were specifically designed to study the coprocessing of coal with 33 W% of "real life" mixed waste plastics, under operating conditions similar to those for Condition 3. Recycle oil to feed ratio was to be increased from 1 to 1.5, depending upon the process requirement. Condition 4 was to feed waste plastics obtained from the Federal Plastics Corporation, in New Jersey. These plastics were the mixed color regrinds of HDPE, PP, and high

impact PS. In the combined feed, 40% HDPE waste, 33% PP waste, and 27% HIPS waste were to be used. Condition 5, on the other hand, was to employ an already mixed form of a plastic waste (more than 95 W% plastics) obtained from a material recovery facility in northern New Jersey, (Monmouth Recycling Company). This particular compacted plastic waste was washed to remove paper and metal scrap and then chipped to a size suitable for addition into the coal-oil slurry.

The actual run plan (Table 2) turned out to be different from the intended run plan, primarily due to issues created by highly viscous feed slurries, which made pumping extremely difficult. Solid-separation by pressure filtrations became increasingly more and more difficult until the middle of the run. This could be due to the type of resid material formed in the presence of dispersed-only catalyst systems. During the first of the intended coal/plastics coprocessing conditions, the "color-regrind" reprocess plastics were found difficult to dissolve in the feed slurry and contributed to nonpumpable highly viscous feed material. As a result of all these operational problems, only three technically meaningful datapoints were obtained. Of these, the first two were the 'coal-only' conditions and studied the effect of HTI's new bimetallic Fe-Mo combined formulation on process performance. The next condition, Condition 3, was a coprocessing condition, utilizing 33 and 25 w% of the "real life" plastic mixed waste from Monmouth Recycling with coal. Due to the plugging problems, the in-line hydrotreater had to be by-passed during Period 17 (Condition 3B).

SYSTEM CONFIGURATION

CMSL-11 involved two equal volume backmixed reactors, a preheater coil, and a fixed-bed in-line hydrotreater. High pressure slurry samples (about 300-500 each) were to be obtained after the first conversion reactor. (Only one such sample, during Period 5, was obtained because of plugging in the later part of the run). A hot-slurry mix tank system was used throughout the run for slurry preparation. Temperatures between 250-450°F were employed for slurry preparation, with slurry viscosities ranging between 1000-3000 cps. No supported catalyst was used in any of the conversion reactors, except in the hydrotreater. A detailed unit configuration/schematic is shown in Figure 1.

COAL AND PLASTICS FEEDS

A subbituminous Black Thunder Mine Coal (HRI-6213), the same coal that was used in PDU 260-005 operations, was used for CMSL-11 (227-89) bench run. Two different plastic feedstocks were obtained for this run: color-regrinds of HDPE, polypropylene, and high impact polystyrene (HIPS) with over 95% purity (obtained from Federal Plastics Recycling). The second source was a "real life" mixed plastic waste obtained from curb-side recycling and donated in compacted form to HTI by Monmouth Recycling. These plastics contained less than 0.1% chlorine; and, for the second source, the composition approximated what is known to exist in a typical municipal solid waste plastic sample (50% HDPE, 33% PP, and 27% PS). The analysis of the coal is shown in Table 3.

START-UP AND MAKE-UP OIL

L-814 : Tank 4 Oil; analysis is shown in Table 3.

CATALYSTS

Hydrotreater:	Criterion C-411 Trilobe (HRI-6135)
Pretreater Coil (to K-1 and K-2):	Molyvan-A, L-845/L-846, and 3 % H ₂ S relative to dry coal.

OPERATIONAL DETAILS

Bench run CMSL-11, as mentioned before, was carried out for seventeen operating days, spread over three run conditions. The numerous operational problems arising out of pumping of highly viscous feeds and plugging of parts of the unit and difficulty of solids separation by pressure filtration were among the reasons for the change in the run plan during the course of operations. Overall, technically meaningful data only was obtained from only three operationally smooth and successful conditions. These covered two 'coal-only' operations and one 'coal-plastics' coprocessing condition. For the entire CMSL-11 run, an average material recovery balance of 96.8 W% was achieved (a tad low). Material balances on a daily basis are plotted in Figure 1 and attached in Appendix. Space velocities and reactor temperatures are plotted in Figures 2 and 4, respectively. The temperatures of both reactors were controlled to their desired values (825-840°F for K-1 and 840-860°F for K-2). The space velocity was adjusted between 40 and 45 lb feed/hr/ft³ reactor to examine its impact on the process performance. Feed composition and dispersed catalyst concentrations are shown in Figures 4 and 5, and relative process thermal severities are shown in Figure 7. The atmospheric still plugged and was taken off-line during Period 8. The pressure filtration became faster and easier in the later part of the run, as plastics were introduced in the feed, and the feed to pressure filtration became lighter due to bypassing of the CAS. The interstage (K-1 slurry) sampling system got plugged during the course of the run, and only one interstage sample, representing Period 5, could be obtained).

PROCESS PERFORMANCE

Detailed laboratory analysis of the products was performed on a daily basis to provide timely process evaluation. The daily material balance, coal conversion, normalized yields and other process performance-related indicators were calculated using programs available in CTSL database. Some programs were modified according to the requirements of the process configuration. Overall process performance during CMSL-11 is summarized in Table 4.

TOTAL COAL CONVERSION

Total coal conversion is calculated on the basis of the solubility of pressure filter solids in quinoline. Coal conversions for different conditions are shown in Figure 7. Throughout the course of the Run 227-89, coal/feed conversions varied between 94.5 W% and 95.5 W% maf. Condition 1, with 5000 ppm of iron and 50 ppm of molybdenum relative to coal, added as HTI's iron catalyst and Molyvan-A, respectively, gave an average coal conversion of over 95 W% maf. As these conversion levels were already high, no improvement in coal conversion was observed at subsequent run conditions. A high conversion (about 95 W% maf) was maintained throughout the run, even during the coal/waste plastics coprocessing conditions.

524°C+ RESIDUUM CONVERSION

The 524° C+ resid conversion represents the ability of the process to convert heavy (high boiling) fractions contained in the feed. For the calculations, all the maf feed coal is considered a 524°C+ resid in the feed. The 524° C+ resid conversion values varied between 84 and 92 W% maf and were more sensitive to the addition of Molyvan-A catalyst, feed composition, and space velocity than to total coal conversion. Resid conversions during each condition are shown in Figure 7. A comparison of process performance between conditions 1 and 2 indicates that the addition of 100 ppm % Mo (50 ppm through Molyvan-A and 50 ppm through HTI's bimetallic Fe-Mo combination) did not significantly affect resid conversion. This may suggest that molybdenum from the bimetallic catalyst is not as effective as Molyvan-A precursor. Therefore, it may make even more sense to stage the addition of dispersed catalysts in future runs in such a manner that both the conversion stages are fed with "fresh" dispersed catalysts, either iron or molybdenum. Resid conversion levels dropped by 5-7% during the coal/waste plastics coprocessing conditions, probably because the refractory high density polyethylene in the plastics did not completely convert to light liquids and gases under the prevailing conditions.

C₄-524°C DISTILLATE YIELDS AND SELECTIVITY

Distillate yields varied between 63 and 68 W%. As shown in Figure 8, distillate yields were not significantly different for the first two 'coal-only' conditions, indicating that there was no apparent advantage of adding 50 ppm molybdenum from HTI's bimetallic formulation to the catalysts employed during Condition 1: 5000 ppm iron from HTI's iron precursor and 50 ppm moly from Molyvan-A. As observed during the coal/plastics coprocessing conditions of the previous bench runs, during CMSL-11 a higher (3-5%) yield of distillate liquids was obtained with both 33 and 25 W% mixed waste plastics in the feed with coal. As high as 67% yields were obtained during the coprocessing conditions. In contrast to the earlier bench runs, the distillates from coal/plastics coprocessing were found to be slightly heavier (Figure 9), indicating a shift to the formation of more heavy distillates (650°F+) in going from 'coal-only' to 'coal-plastics' coprocessing conditions. This could be due to the types of plastics in the "real life" mixture being different from the virgin plastics employed during the prior bench runs.

HYDROGEN CONSUMPTION

Hydrogen consumption based on the mf feed varied between 3.9 and 6.5 W%. Chemical hydrogen consumption was at similar levels for the first two run conditions. As shown in Figure 10, the consumption decreased significantly during coal/waste plastics coprocessing. This observation, which is similar to results from the earlier bench runs with coal/waste plastics coprocessing, confirms our hypothesis that the presence of 25-33 W% mixed waste plastics in the feed with coal improves hydrogen utilization and makes the overall process more hydrogen efficient.

C₁-C₃ GAS YIELDS

As shown in Figure 10, the normalized C₁-C₃ gas yield for CMSL-11 varied between 7.1 and 17.2 W%. During the 'coal-only' conditions (Conditions 1 and 2), the light gas yields were very high (15-17 %), probably as a result of high process severity. Indeed, it is believed that the thermal severity of the process during the 'coal-only' liquefaction conditions should be reduced in order to optimize product distribution and, light distillate selectivity. Light gas yield dropped significantly during coal/plastics coprocessing. This decrease was more than the proportion of waste plastics in the feed, indicating that the presence of plastics in the feed leads to the reduction in the light gas formation from coal.

PRODUCT QUALITY

Products of different fractions (First-Stage/Second-Stage Vent Gases, CAS Bottoms, SOH, PFL and PFS/VSB) from work-up periods 5, 10, 16 and 17 were analyzed in detail. The results of these analyses are summarized in Tables 6 through 8.

Separator Overhead Product (SOH)

The SOH oil stream represents the net light distillate (IBP-750°F) from CMSL-11. The properties of SOH oil for the work-up periods are shown in Table 6. SOH oil had a typical boiling range of 130-750°F. IBP-350°F, the lightest fraction of the SOH oil, was highest for Condition 2, employing 100 ppm molybdenum with 5000 ppm iron. The API gravities (an indication of paraffinic character) of the SOH oil were high (>34). The heteroatoms level (nitrogen and sulfur) were below 50 ppm throughout the run, indicating very successful operation of the in-line hydrotreater. In fact, during Period 17, when the HTU had to be by-passed due to plugging problems, the heteroatom contents of the SOH distillates were much higher (3677 ppm nitrogen and 4861 ppm sulfur) than when the HTU was operating. The H/C ratio of the SOH oil was also lower during Period 17. During the coal-plastics coprocessing Period 16, a slight decrease in the lightest boiling fraction of the SOH oil was observed, even though the API gravity of this SOH oil was the highest, indicating a more paraffinic nature.

Pressure Filter Liquid (PFL)

Pressure filter liquid (PFL) represents the liquid (oil) fraction of the atmospheric still (CAS) bottoms. In CMSL-11, CAS bottoms was not used as recycle solvent; only the solids-free PFL was used to constitute the recycle oil. As shown in Table 7, PFL has a broad boiling range. As shown in Figure 11, the toluene insoluble fraction of the PFL varied from 8 to 13 W% while cyclohexane insolubles varied from 21 to 28 W%. The yield of the high boiling fraction (524°C+) varied from 30 to 37 W%, depending on process conditions and feed composition. A large portion of the 524°C+ PFL was toluene soluble (70 W%).

EXTERNAL SAMPLES

As mentioned earlier, a number of samples of different process streams from CMSL-11 were obtained (for further detailed characterization and products assessment) for Consol, Inc. and also for members of the Consortium of Fossil Fuel Liquefaction Science. These samples, their amounts, and the operating periods when there were withdrawn are shown in Table 9.

CONCLUSIONS

The following specific conclusions are drawn based upon the results from Bench Run CMSL-11:

1. Molybdenum, added to coal liquefaction reactor in the form of HTI's bimetallic catalyst, was not as effective a catalyst as a separately added Molyvan-A precursor.
2. Coprocessing of coal with waste plastics improved the light distillate yields by as much as 5 % while at the same time reducing the light hydrocarbon gas make and hydrogen consumption.
3. The "real life" waste plastics (which primarily consisted of HDPE), used for the first time at HTI during CMSL-11, resulted in a different type of product slate (and distillate distribution) with coal than the "simulated" co-mingled plastics which was coprocessed with coal during the earlier bench runs.
4. In-line hydrotreater resulted in distillate oil containing less than 50 ppm nitrogen and sulfur and with an H/C atomic ratio of over 1.7.

RECOMMENDATIONS FOR FUTURE WORK

Based upon the results from bench run CMSL-11, it is strongly recommended that the combined bimetallic dispersed catalyst system, consisting of iron and small amounts of molybdenum, be looked at more closely efforts must be made during catalyst preparation to improve the dispersion of molybdenum on the iron catalyst. As CMSL-11 was the first bench operation at HTI that employed "real life" municipal solid waste plastics coprocessing with coal, problems associated with the inherent heterogeneity of these plastics were experienced. These variable waste plastics compositions make it extremely difficult to quantitatively study the effects of process variables on overall process performance. The operation of the continuous unit, especially in the feed section, is also rendered uneven. Therefore, it is recommended that either a "representative waste plastics mix" be obtained from American Plastics Council/Plastics Recycling Foundation for feed or the use of "virgin" plastics of a known compositional mix be restarted.

TASK 4- TECHNICAL ASSESSMENT

Technical assessment and economic analysis were performed on the last three CMSL-runs in this during the reporting period. These three CMSL runs investigated liquefaction in an all-dispersed-catalyst system with coal and coal/plastics mixtures. The coal in each run was subbituminous, and the plastics were mixtures of polyethylene, polystyrene, and polypropylene. The plastics content of the total liquefaction feed varied from zero to fifty percent. The dispersed catalyst was a mixture of Molyvan A and Iron.

CMSL-9 was carried out at constant reactor operating conditions and used Molyvan rates of 100 to 300 ppm and an Iron rate of 10,000 ppm when plastics were fed. The plastics content of the feed varied from 0 to 50%. The economics presented in Table 10 show a clear advantage for incorporating plastics in the liquefaction feed. The equivalent crude oil price is significantly lower with plastics than with coal-only operation with dispersed catalyst or with supported catalyst (base case). The economics assumed no cost for plastics, but even in the \$20 to \$40/ton price range the use of plastics mixtures is favored over coal-only liquefaction, as seen in Figure 12. The economic effect of dispersed catalyst rate is shown in Figure 13, which indicates favorable economics over supported catalyst at iron catalyst rates below 5,000 ppm.

CMSL-10 was performed in a coal-only mode, with varying space velocities. Dispersed catalyst rates were lowered from those used in CMSL-9 to 100 ppm Molyvan and 5,000 ppm Iron. The results in Table 11 show that despite the lower liquid product, there is a clear economic benefit in operating at higher space velocity, both in terms of reduced plant investment and in a lower equivalent crude oil price. Operation with dispersed catalyst is an economic standoff with the supported catalyst base case at the same space velocity.

CMSL-11 was performed at the higher space velocity and the lower dispersed catalyst rates previously demonstrated in CMSL-10. Plastics content of the feed varied from 0 to 33%. The results, listed in Table 12, again demonstrate the economic benefit of using coal/plastics mixtures, compared to coal-only operation, using either dispersed catalyst (Period 9) or supported catalyst (base case).

TASK 5- PROJECT MANAGEMENT

Two papers were presented during this reporting quarter, one at the DOE Contractors' Review Meeting held in Pittsburgh, PA, and another at the CFFLS Ninth Annual Meeting held in Pipestem, WV, both during August 1995. The final topical report on the CMSL Project is being compiled and will be submitted to DOE by December 15, 1995. The final topical report will be divided in three volumes- (I) Project Overview and Technical Assessment, (II) Direct Coal Liquefaction Runs CMSL-01 thru' 07, and (III) Coal/Waste Plastics Coprocessing Runs CMSL-08 thru' CMSL-11.

TABLE 2

CMSL-11 MODIFIED (ACTUAL) RUN PLAN

Black Thunder Coal (HRI-6213: POC-02 coal, dried to about 11% moisture)

Back Pressure: 2500 psig (17.3 MPa)

Catalyst: Dispersed Fe and Mo Catalysts & C-411 in HTU

Condition	1	2	3A	3B
Period	1-5	7B-10	13-16	17
W-up Periods	5	10	16	17**
Temperatures, C				
Pretreater Coil	301	301	301	301
Reactor K-1	441	441	449	449
Reactor K-2	449	449	460	460
Hydrotreater	379	379	379	379
Space Velocity	640	640	720	720
[kg coal/h/m ³ reactor]				
Solvent/Feed Ratio	1	1	1.5	1.5
Dispersed Catalysts, ppm				
HTI Fe Catalyst	5000	5000	5000	5000
Molyvan-A	50	50	50	50
Mo from HTI Fe-Mo	0	50	50	50
bimetallic catalyst				
W% coal in Feed	100	100	67	75
W% Plastics in Feed*	0	0	33	25
H ₂ S RATE	-----3 W% OF DRY COAL-----			

*Conditions 3A and 3B used the actual mixed plastics waste from an MSW recovery facility in northern NJ.

** In-line hydrotreater was bypassed during Period 17 due to plugging problems.

TABLE 3

CMSL-11 INTENDED RUN PLAN

Black Thunder Coal (HRI-6213: POC-02 coal, dried to about 11% moisture)

Back Pressure: 2500 psig (17.3 MPa)

Catalyst: Dispersed Fe and Mo Catalysts & C-411 in HTU

Condition	1	2	3	4	5
Period	1-5	6-8	8-10	11-13	14-16
W-up Periods	5	8	11	14	16
Temperatures, C					
Pretreater Coil**	301	301	302	302	302
Reactor K-1	441	441	449	449	449
Reactor K-2	449	449	460	460	460
Hydrotreater	379	379	379	379	379
Space Velocity	640	640	720	720	720
[kg coal/h/m ³ reactor]					
Solvent/Feed Ratio	1	1	1	1.5	1.5
Dispersed Catalysts, ppm					
HTI Fe Catalyst	5000	5000	5000	5000	5000
Molyvan-A	50	00/50****	100	100	100
W% coal in Feed	100	100	100	67	67
W% Plastics in Feed***	0	0	0	33	33
H ₂ S RATE	-----3 W% OF DRY COAL-----				

*HTU will be by-passed during Periods 6 and 15A.

** The residence time in the pretreater coil will be maintained at about five minutes.

***Condition 4 will use waste plastics obtained from Federal Plastics Corporation, which are mixed color re-grinds of HDPE, PP, and high impact PS.

Condition 5 will use the actual mixed plastics waste from an MSW recovery facility in northern NJ.

****Instead of using 50 ppm Mo from Molyvan-A, molybdenum, incorporated in the HTI's iron catalyst will be used during Condition 2.

Note: Conditions 3 through 5 will employ HTI's Fe-Mo-S Catalyst at 5000 ppm Fe and 50 ppm Mo; in addition Molyvan-A will also be

TABLE 4

Run CMSL-11 Process Performance Summary*

Condition	1	2	3A	4B
Period Number	5	10	16	17
Hours of Run	120	240	384	408
Dispersed Catalyst ppm*: Fresh Mo	50	100	100	100
Fresh Iron	5000	5000	5000	5000
W% Waste Plastics Feed	0	0	33	25
SV, Kg Coal/hr/m ³	703	671	687	662
SV, Lb Coal/hr/ft ³	43.9	41.9	42.9	41.3
Temperatures, °C				
Pretreater Coil	----- 302 -----			
First Stage	441	450	450	447
Second Stage	449	459	459	461
Relative Process Severity	1.00	1.15	1.14	1.14
Material Balance (%) (gross)	96.65	102.82	99.37	95.63
Estimated Normalized Yields, W% Dry Feed:				
C1-C3 in Gases	14.76	17.17	8.29	7.09
C4-C7 in Gases	4.84	8.07	4.61	3.73
IBP-177°C in Liquids	14.88	12.41	11.63	9.08
199-260°C in Liquids	13.51	11.66	9.71	10.49
260-343°C in Liquids	18.62	14.41	14.15	14.47
343-454°C in Liquids	8.34	10.49	19.13	21.32
454-524°C in Liquids	0.68	2.27	5.19	5.57
524°C+	3.72	5.68	10.95	10.68
Unconverted Feed	4.22	4.58	4.54	5.1
Water	9.31	7.28	9.33	11.14
CO _x	6.97	6.38	2.80	1.9
NH ₃	0.97	0.92	0.51	0.58
H ₂ S	-0.02	-0.57	-0.92	-0.74
Hydrogen Consumption	6.53	6.51	3.85	4.73
Process Performance, W% MAF Feed				
Coal Conversion	95.5	95.1	95.3	94.7
C4-524°C Distillate Yield	64.6	62.9	67.0	67.6
524°C+ Conversion	91.5	89.1	83.9	83.5

*This table includes the performance data only from the Conditions of CMSL-11 which were operationally smooth and successful.

TABLE 5

Dispersed Catalysts: Process Performance Comparisons

Unit	227	227	227
Run	89	88	87
Run ID	CMSL-11	CMSL-10	CMSL-9
Period Number	10	14	15
Hours of Run (end of period)	240	336	360
Dispersed Catalyst ppm: Fresh Mo	100	100	150
Fresh Iron	5000	5000	0
Recycled Mo	0	0	150
First Stage SV, Kg Coal/hr/m ³	671	655	659
First Stage SV, Lb Coal/hr/ft ³	41.9	40.9	41.1
Temperatures, °C			
Pretreater Coil	302	304	302
First Stage	450	444	445
Second Stage	459	451	450
Relative Process Severity	1.00	0.90	0.89
Material Balance (%) (gross)	102.82	102.2	98.5
Estimated Normalized Yields, W% Dry Feed:			
C1-C3 in Gases	17.17	12.20	12.08
C4-C7 in Gases	8.07	4.56	4.96
IBP-177°C in Liquids	12.41	12.81	14.26
199-260°C in Liquids	11.66	9.69	14.62
260-343°C in Liquids	14.41	13.96	15.71
343-454°C in Liquids	10.49	12.73	6.77
454-524°C in Liquids	2.27	3.39	2.26
524°C+	5.68	8.60	5.78
Unconverted Feed	4.58	5.16	4.55
Water	7.28	10.96	13.22
Co _x	6.38	5.63	5.59
NH ₃	0.92	0.86	0.97
H ₂ S	-0.57	-0.19	0.16
Hydrogen Consumption	6.51	6.12	6.69
Process Performance, W% MAF Feed			
Coal Conversion	95.1	94.5	95.2
C4-524°C Distillate Yield	62.9	60.9	62.2
524°C+ Conversion	89.1	85.4	89.0

TABLE 6**Separator Overhead (SOH) Properties**

Condition	1	2	4	4
Period	5	10	16	17
Gravity °API	32.9	35	38.1	31.6
IBP, °C	58	56	57	59
FBP, °C	376	370	387	410
Elemental Analysis				
Carbon, W%	86.9	87.4	86.1	85.3
Hydrogen, W%	12.3	12.65	12.9	11.5
Sulfur (Antek), ppm	22.3	45.4	48.4	4861
Nitrogen (Antek), ppm	145.2	68.1	50.2	3677
H/C Ratio	1.69	1.74	1.79	1.62
ASTM D-86 Distillation, Composition, W%				
IBP-177°C	28.3	34.1	31.4	24.4
199-260°C	26.1	30.5	25.9	28.3
260-343°C	34.3	27.8	32	28.7
343°C+	10.4	7.2	10.1	17.8
LOSS	0.9	0.4	0.6	0.8

TABLE 7**Properties of the Pressure Filter Liquids (Second Stage)**

Condition	1	2	4	4
Period	5	10	16	17
Gravity °API	-10.1	-8.3	3.4	0.9
IBP, °C	272	229	268	234
Elemental Analysis, W%				
Carbon	85.2	87.0	88.4	88.7
Hydrogen	6.9	7.0	8.9	8.8
Sulfur	1.2	0.8	1.1	1.0
Nitrogen	0.9	1.1	0.5	0.5
H/C Ratio	1.0	1.0	1.2	1.2
ASTM D-86 Distillation, Composition, W%				
IBP-343°C	6.8	15.4	7.2	11.2
343-454°C	41.8	39.4	45.1	42.1
454-524°C	13.6	12.0	15.2	15.8
524°C+	37.6	33.0	32.0	30.3
LOSS	0.2	0.2	0.5	0.6
Cyclohexane Insolubles, W%	27.6	28.2	21.1	24.2
Toluene Insolubles, W%	13.1	10.6	10.5	8.4

TABLE 8**Inspection of the Pressure Filter Solids (Second Stage)**

Condition	1	2	4	4
Period	5	10	16	17
Elemental Analysis, W%				
Carbon	56.3	53.1	49.6	47.5
Hydrogen	4.0	3.6	3.6	3.1
Sulfur	3.5	4.7	5.3	5.4
Nitrogen	0.6	0.6	0.7	0.9
H/C Ratio	0.8	0.8	0.9	0.8
Composition, W%				
Quinoline Insolubles	53.1	54.7	63.3	64.9
Ash (Quinoline Filtration)	37.2	40.0	37.3	38.2
Sulfur in Ash	7.1	9.5	8.5	8.9
ASTM Ash	37.4	38.8	37.7	40.2
Sulfur in Ash	7.1	8.1	6.6	7.7
Coal Conversion, W% MAF	95.5	95.1	95.3	94.7

TABLE 9

Hydrocarbon Technologies, Inc.

SHIPPING REQUEST FORM

<u>Requested By :</u> Vivek Pradhan	<u>Need Date</u> 09/25/95	<u>WO Number</u> 846-120	<u>Date Sub.</u> 09/15/95																							
<p><u>Sample Description & Amounts:</u></p> <table style="width: 100%;"> <tr> <td></td> <td style="text-align: right;"><u>File with:</u> 227-89</td> </tr> </table> <table style="width: 100%;"> <tr> <td style="width: 40%;">1. FEED SLURRY</td> <td style="width: 20%; text-align: right;">250 GM</td> <td style="width: 40%;">PERIODS 5, 10, 16</td> </tr> <tr> <td>2. CAS BOTTOMS</td> <td style="text-align: right;">350 GM</td> <td>PERIODS 5, 10, 16</td> </tr> <tr> <td>3. SOH OIL</td> <td style="text-align: right;">250 GM</td> <td>PERIODS 5, 10, 16, 17</td> </tr> <tr> <td>4. ASOH MATERIAL</td> <td style="text-align: right;">250 GM</td> <td>PERIOD 5 only</td> </tr> <tr> <td>5. PRESSURE FILTER LIQUID</td> <td style="text-align: right;">350 GM</td> <td>PERIODS 5, 10, 16</td> </tr> <tr> <td>6. PRESSURE FILTER SOLID</td> <td style="text-align: right;">350 GM</td> <td>PERIODS 5, 10, 16</td> </tr> <tr> <td>7. INTERSTAGE (K-2) SLURRY</td> <td style="text-align: right;">350 GM</td> <td>PERIOD 5 only</td> </tr> </table>					<u>File with:</u> 227-89	1. FEED SLURRY	250 GM	PERIODS 5, 10, 16	2. CAS BOTTOMS	350 GM	PERIODS 5, 10, 16	3. SOH OIL	250 GM	PERIODS 5, 10, 16, 17	4. ASOH MATERIAL	250 GM	PERIOD 5 only	5. PRESSURE FILTER LIQUID	350 GM	PERIODS 5, 10, 16	6. PRESSURE FILTER SOLID	350 GM	PERIODS 5, 10, 16	7. INTERSTAGE (K-2) SLURRY	350 GM	PERIOD 5 only
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<p><u>Special Instructions:</u></p> <p>[PLEASE ENCLOSE THE MSDS INFORMATION WITH THE SHIPMENT]</p>																										
<p><u>WHERE DO SAMPLES GO?</u></p> <p>Attention: DR. GARY ROBBINS CONSOL, INC. R & D 400 BROWNSVILLE ROAD LIBRARY, PA 15129.</p>																										

TABLE 10

CMSL - 9

Coal/Plastics Operation, All-Dispersed-Catalyst System

Summary of Economics

Case	Base	Period 5	Period 34	Period 41
Percent Plastics in Feed	0	0	33	50
<u>Feed, T/D</u>				
Coal	10,500	10,500	7,000	5,250
Plastics	0	0	3,500	5,250
Total	10,500	10,500	10,500	10,500
<u>Liquid Products, B/D</u>				
Gasoline	15,067	12,329	13,837	13,540
Diesel Fuel	36,591	29,944	33,605	32,884
Total	51,658	42,273	47,442	46,424
Barrels of Liquid per Ton of Feed	4.92	4.03	4.52	4.42
Total Plant Investment Cost(1)	2,494	2,491	2,245	2,075
Cost, \$/daily barrel of Product	48,283	58,934	47,329	44,688
Net Annual Product Cost, \$MM	567.39	506.53	499.04	448.25
Net Product Cost, \$/B	33.44	36.48	32.02	29.39
Equivalent Crude Price, \$/B	27.40	30.39	26.04	23.54

(1) Millions of dollars, 1991 US Gulf Coast basis

TABLE 11

CMSL - 10
Coal-only Operation, All-Dispersed-Catalyst System
Summary of Economics

Case	Base	Period 9	Period 18
Space Velocity, lb/hr/ft ³ reactor	45	26	45
Feed, T/D	10,500	10,500	10,500
<u>Liquid Products, B/D</u>			
Gasoline	11,787	11,701	11,482
Diesel Fuel	28,626	28,418	27,886
Total	40,413	40,119	39,368
Barrels of Liquid per Ton of Feed	3.85	3.82	3.75
Total Plant Investment Cost(1)	2,354	2,658	2,302
Cost, \$/daily barrel of Product	58,254	66,258	58,479
Net Annual Product Cost, \$MM	494.90	547.45	487.06
Net Product Cost, \$/B	37.28	41.54	37.66
Equivalent Crude Price, \$/B	31.20	35.56	31.58

(1) Millions of dollars, 1991 US Gulf Coast basis

TABLE 12

CMSL - 11
Coal/Plastics Operation, All-Dispersed-Catalyst System
Summary of Economics

Case	Base	Period 10	Period 16
Percent Plastics in Feed	0	0	33
<u>Feed, T/D</u>			
Coal	10,500	10,500	7,000
Plastics	0	0	3,500
Total	10,500	10,500	10,500
<u>Liquid Products, B/D</u>			
Gasoline	11,787	11,527	12,030
Diesel Fuel	28,626	27,995	29,217
Total	40,413	40,119	41,247
Barrels of Liquid per Ton of Feed	3.85	3.76	3.93
Total Plant Investment Cost(1)	2,354	2,579	2,091
Cost, \$/daily barrel of Product	58,254	65,255	50,702
Net Annual Product Cost, \$MM	494.90	533.56	429.03
Net Product Cost, \$/B	37.28	41.10	31.66
Equivalent Crude Price, \$/B	31.20	35.10	25.69

(1) Millions of dollars, 1991 US Gulf Coast basis

FIGURE 1

CMSL-11: Daily Material Balances

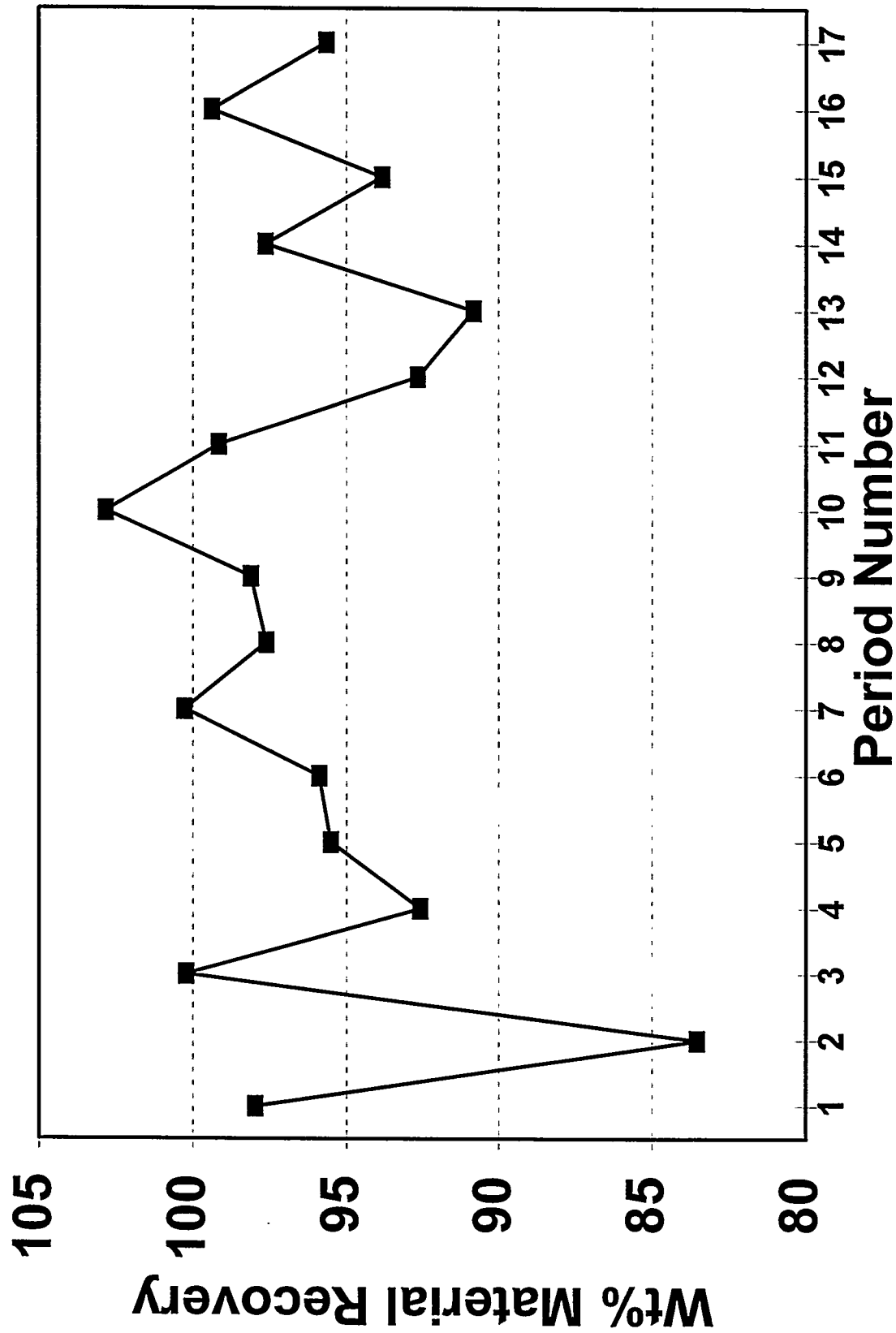


FIGURE 2.

CMSL-11: Daily Feed Space Velocities

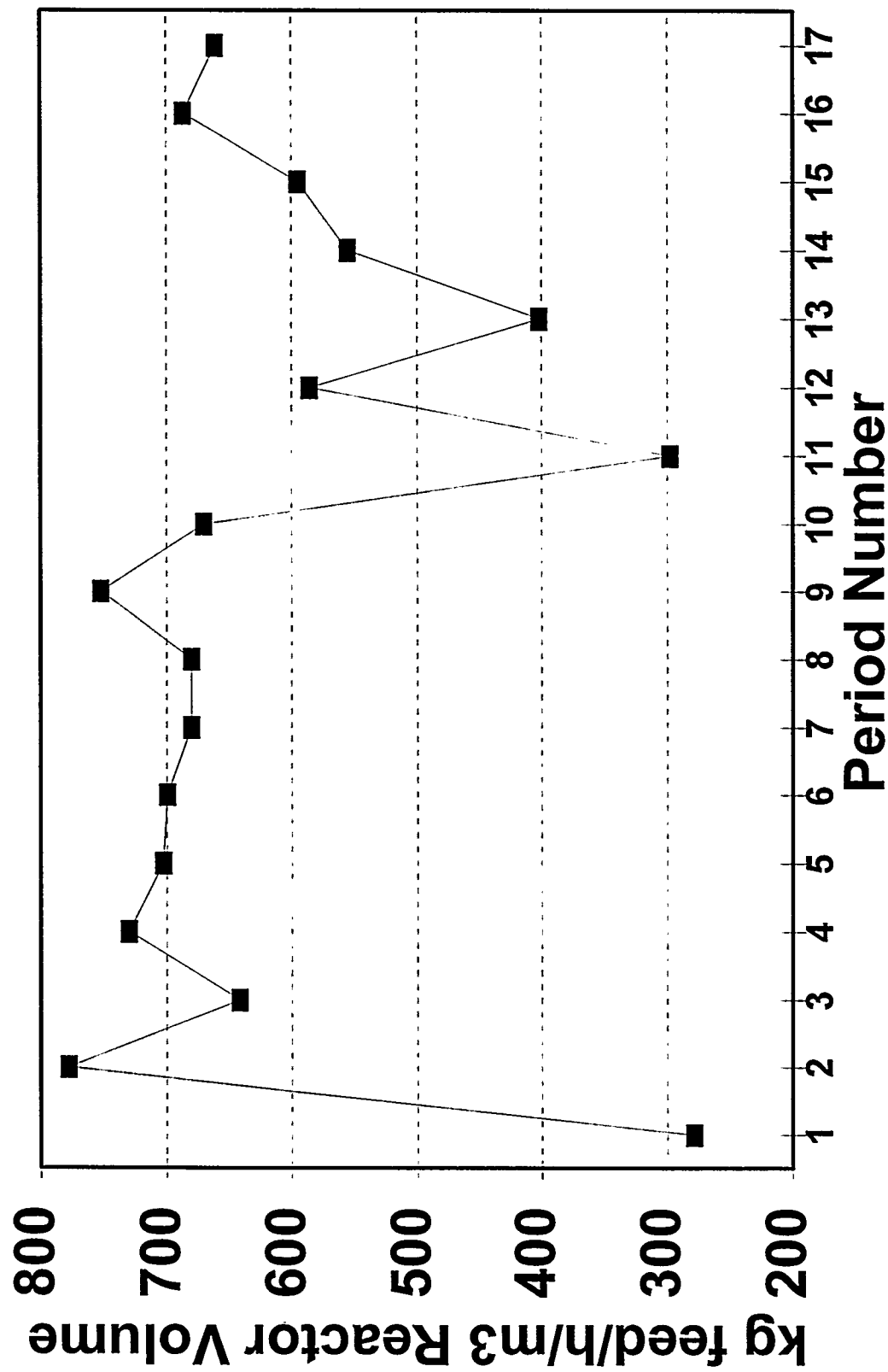


FIGURE 3

CMSL-11: Daily Reactor Temperatures

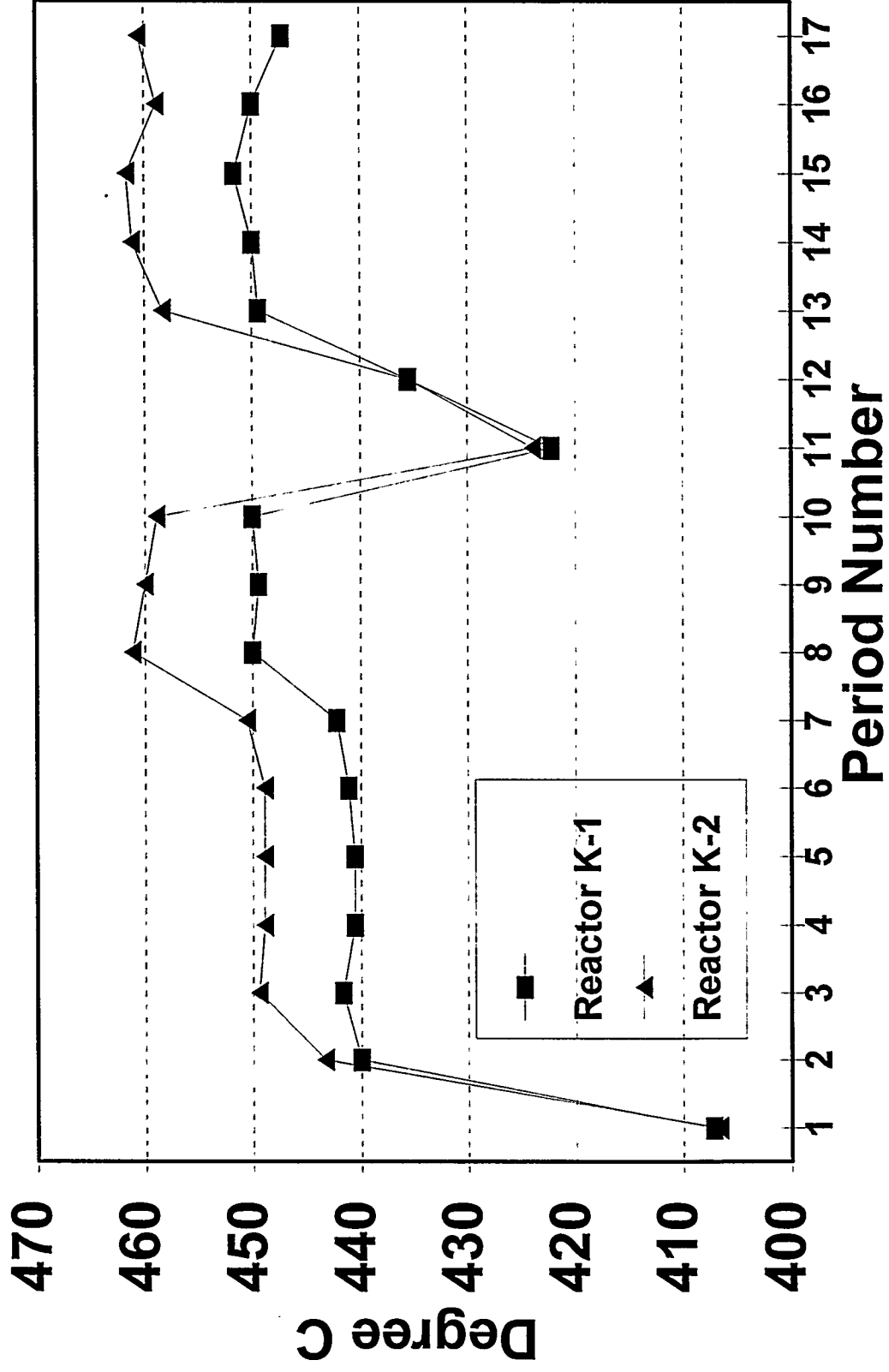


FIGURE 4

CMSL-11: Feed Composition

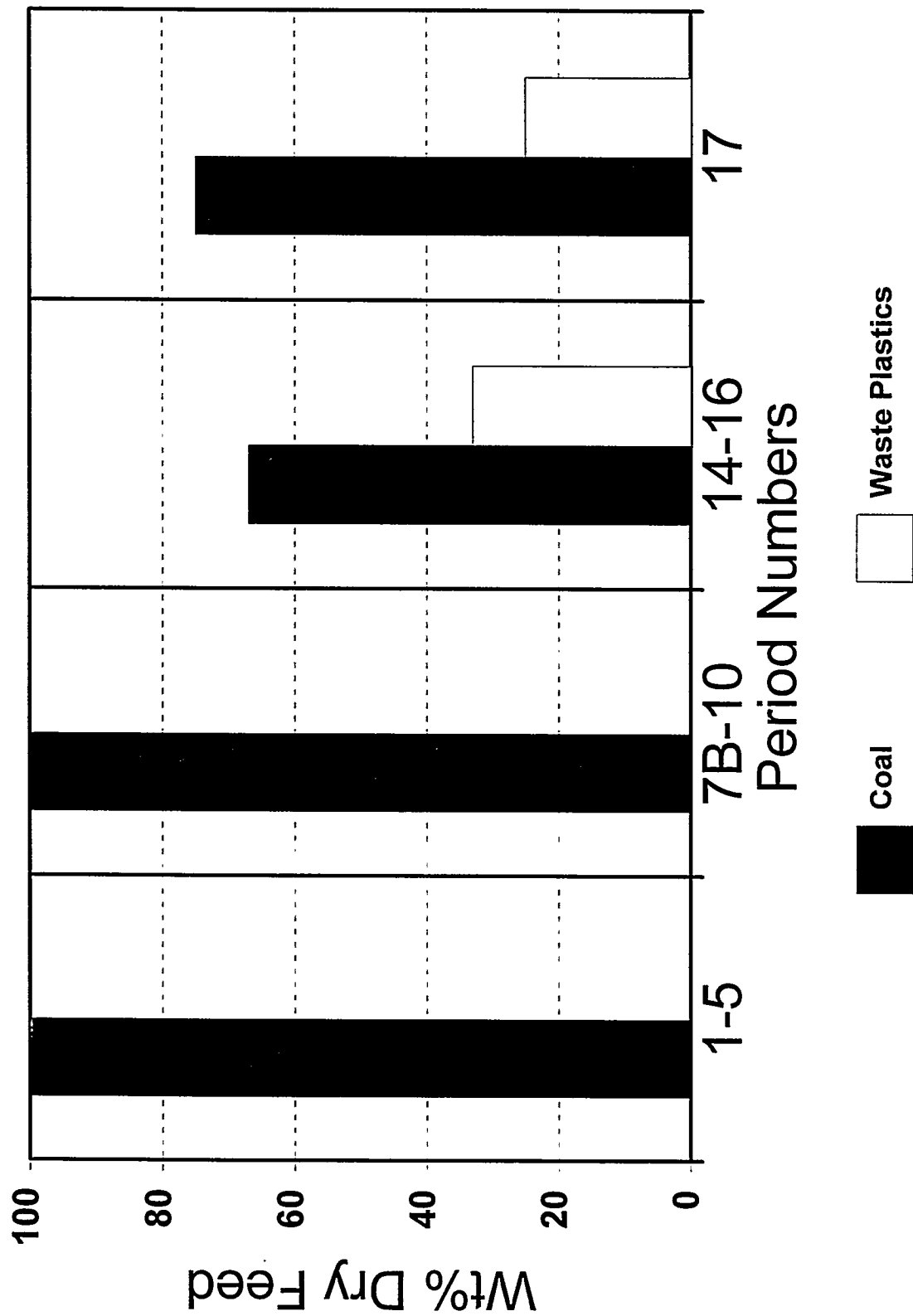


FIGURE 5

CMSL-11: Conditions vs. Catalysts Conc

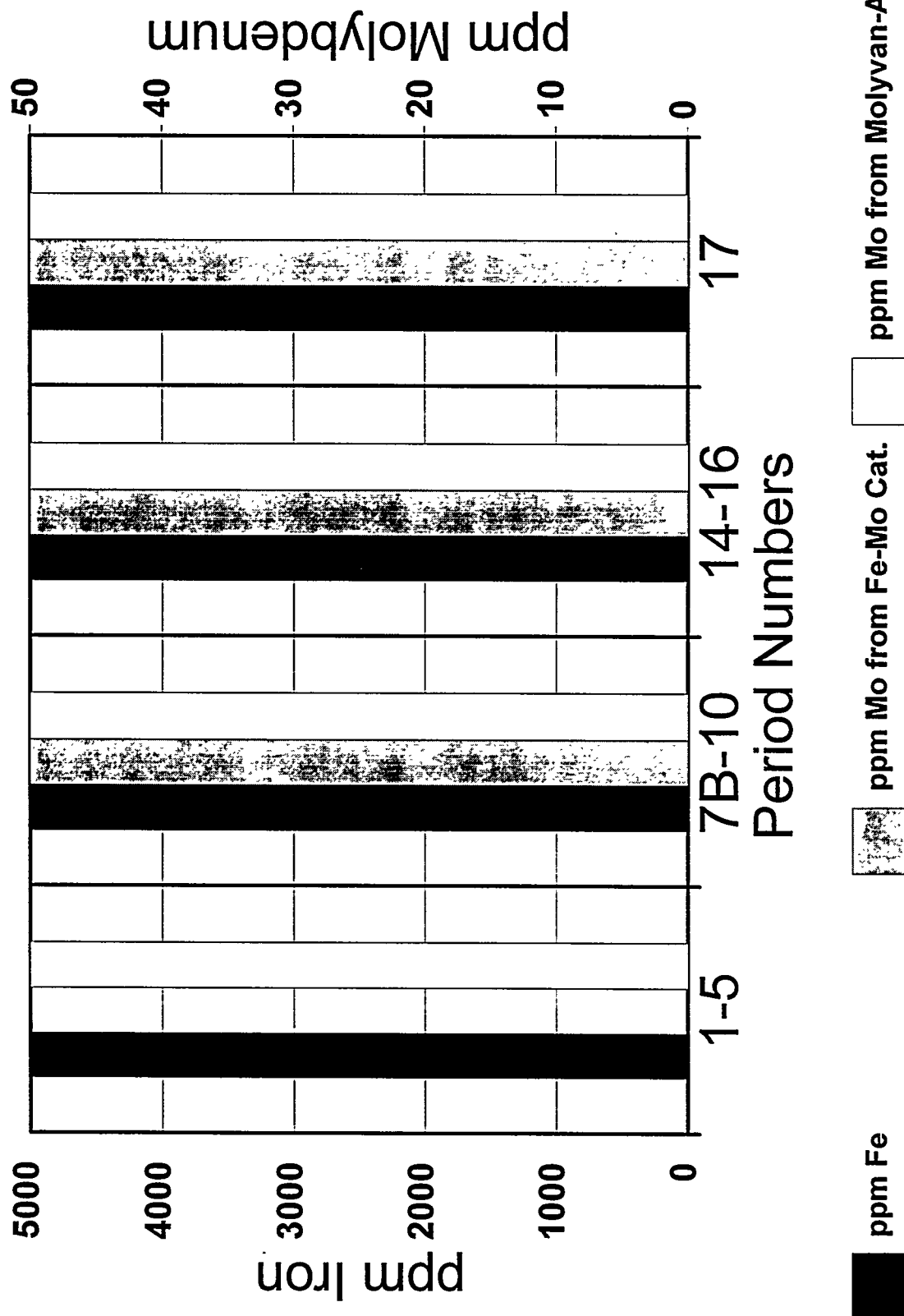


FIGURE 6

CMSL-11: Relative Thermal Severity

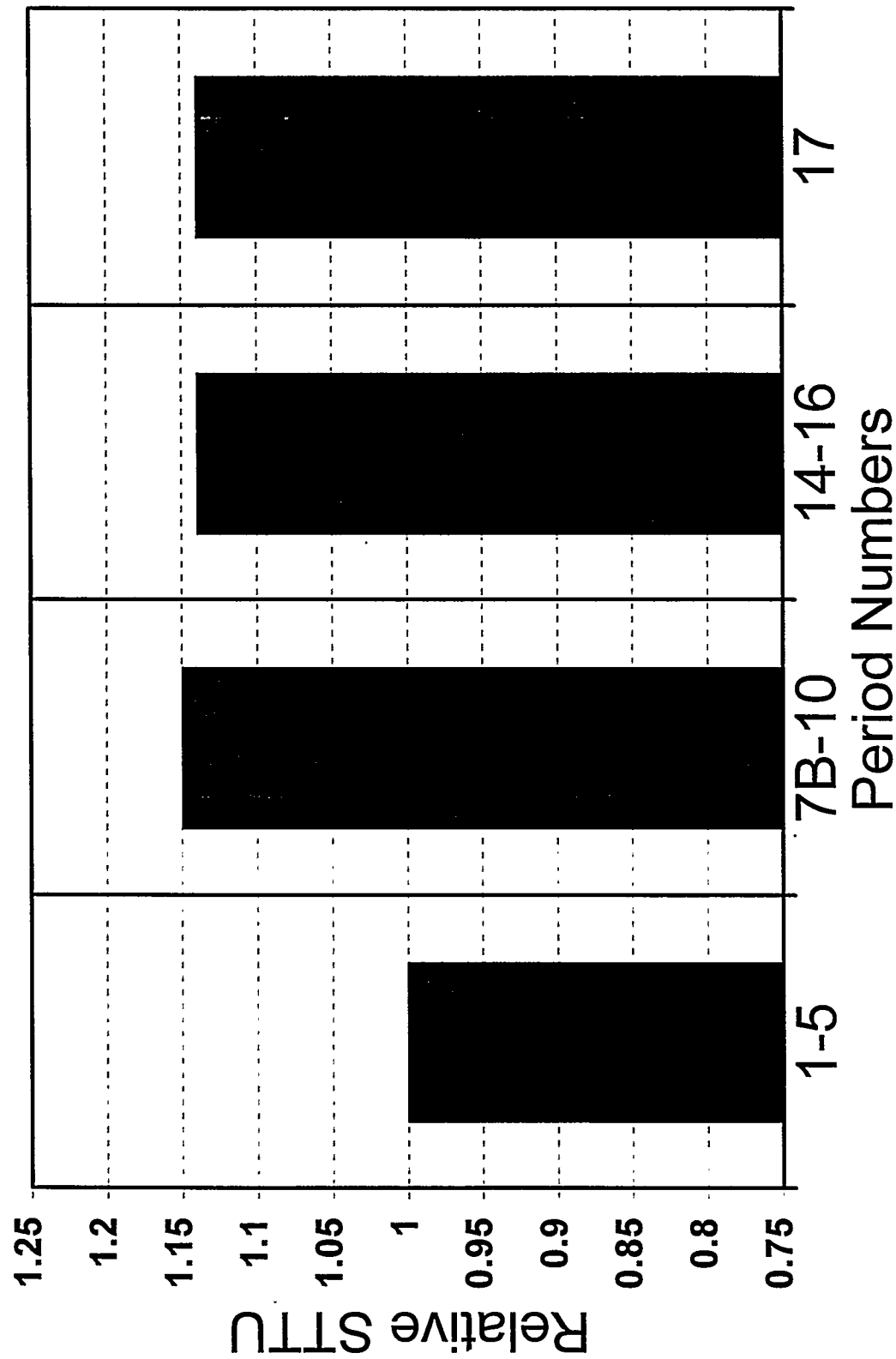


FIGURE 7

CMSL-11: Feed & Resid Conversions

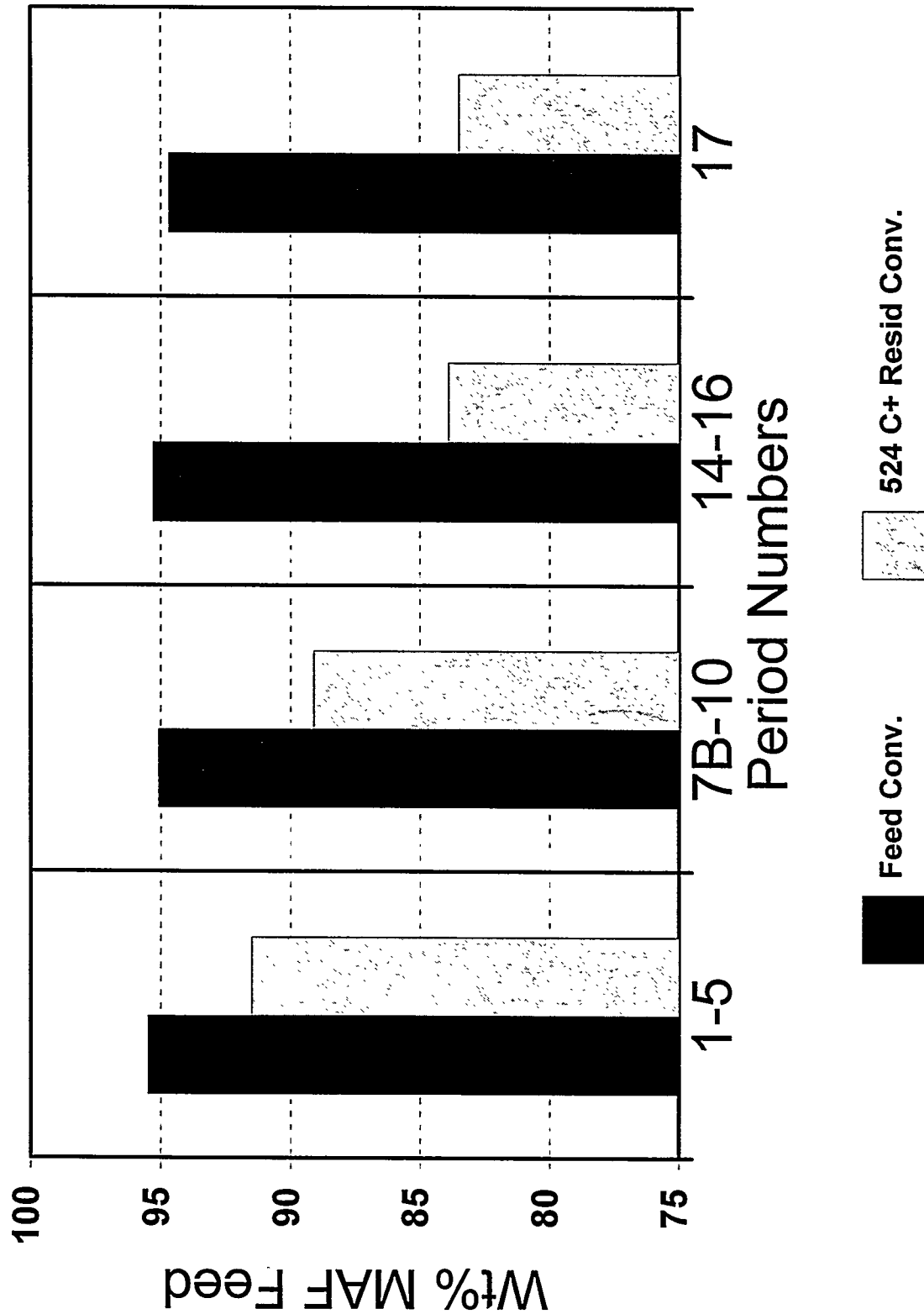


FIGURE 8

CMSL-11: C4-524 C Liquid Yield

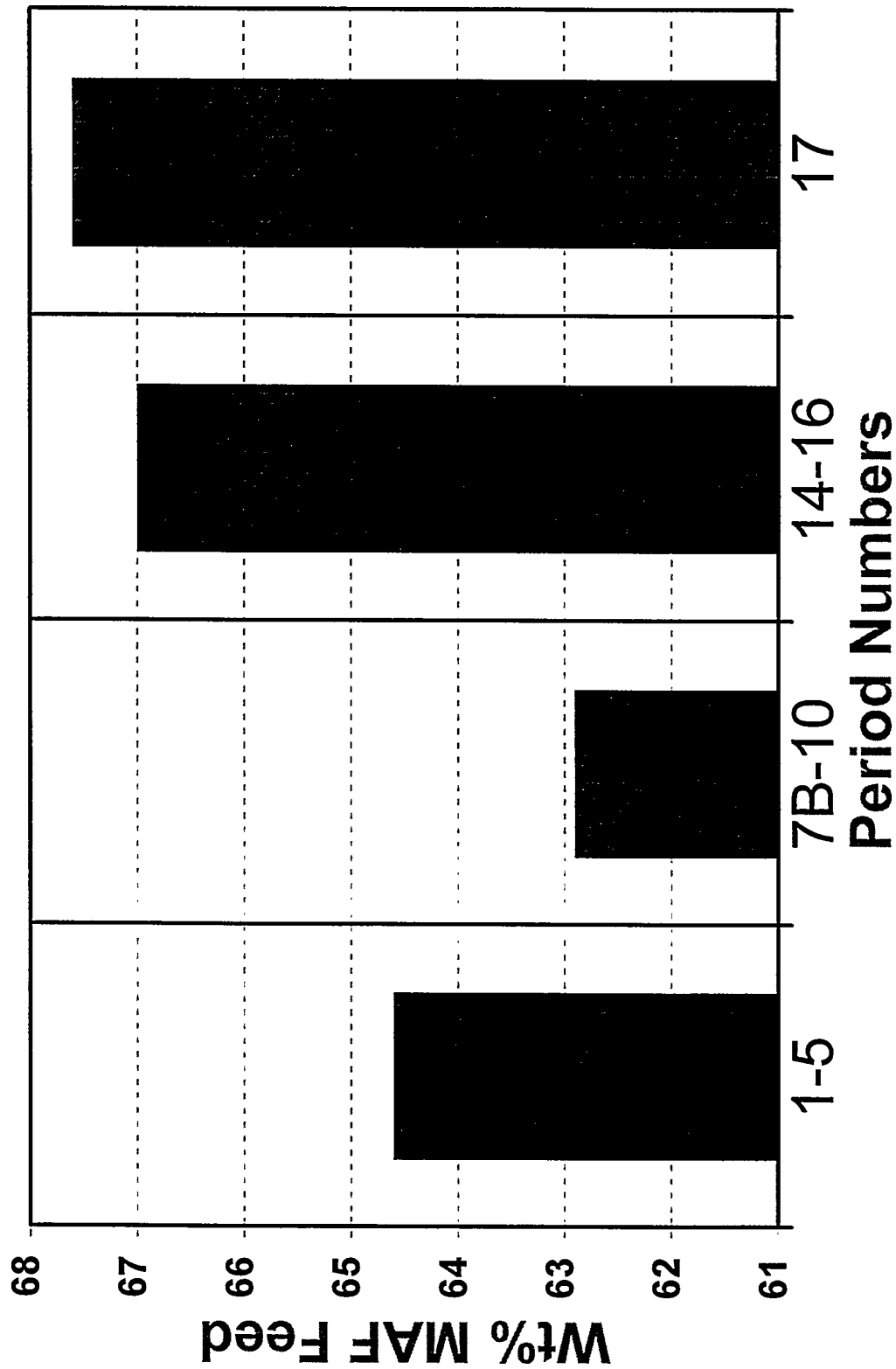


FIGURE 9

CMSL-11: Distillate Selectivity

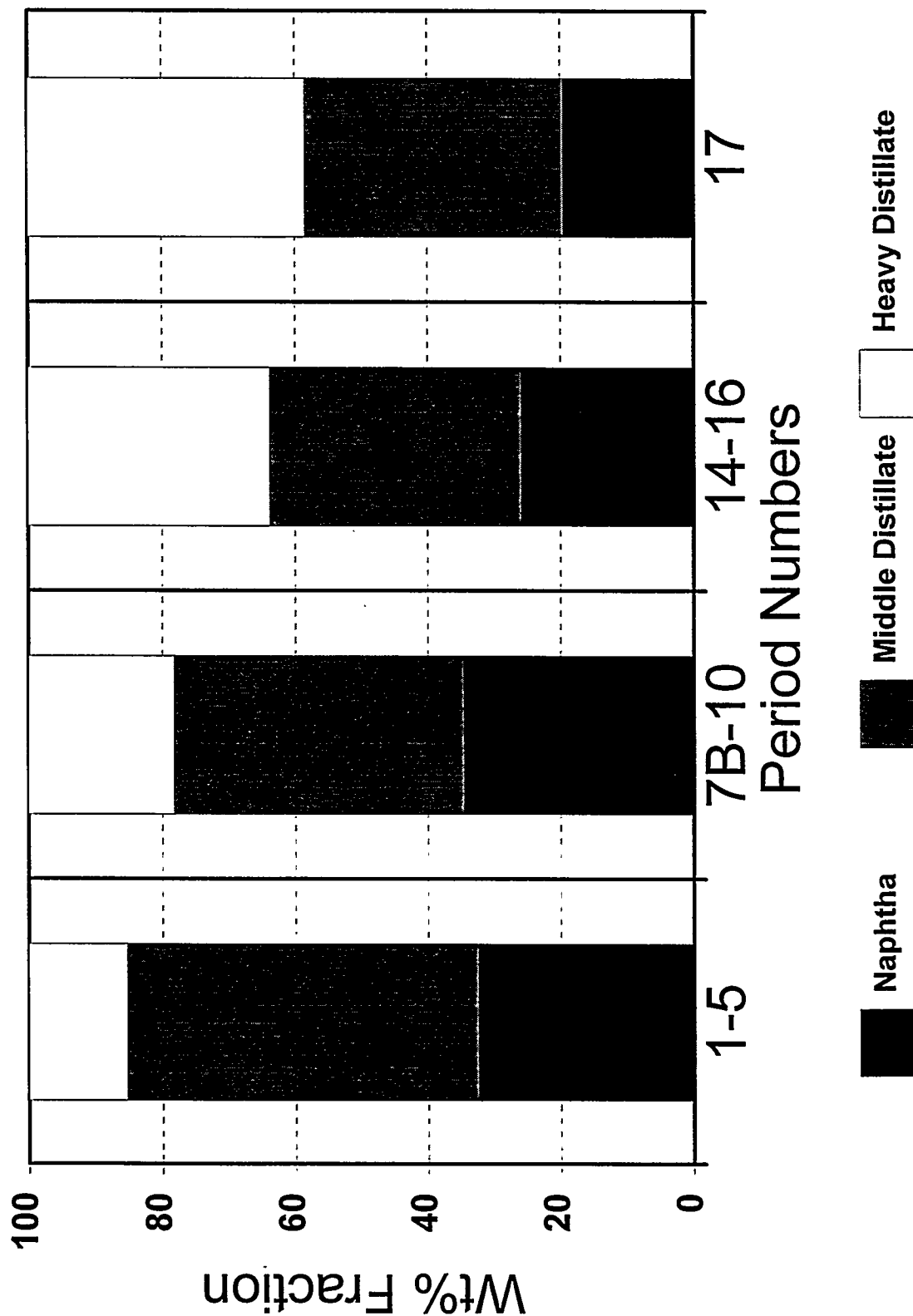


FIGURE 10

CMSL-11: Gas Yield/H₂-Consumption

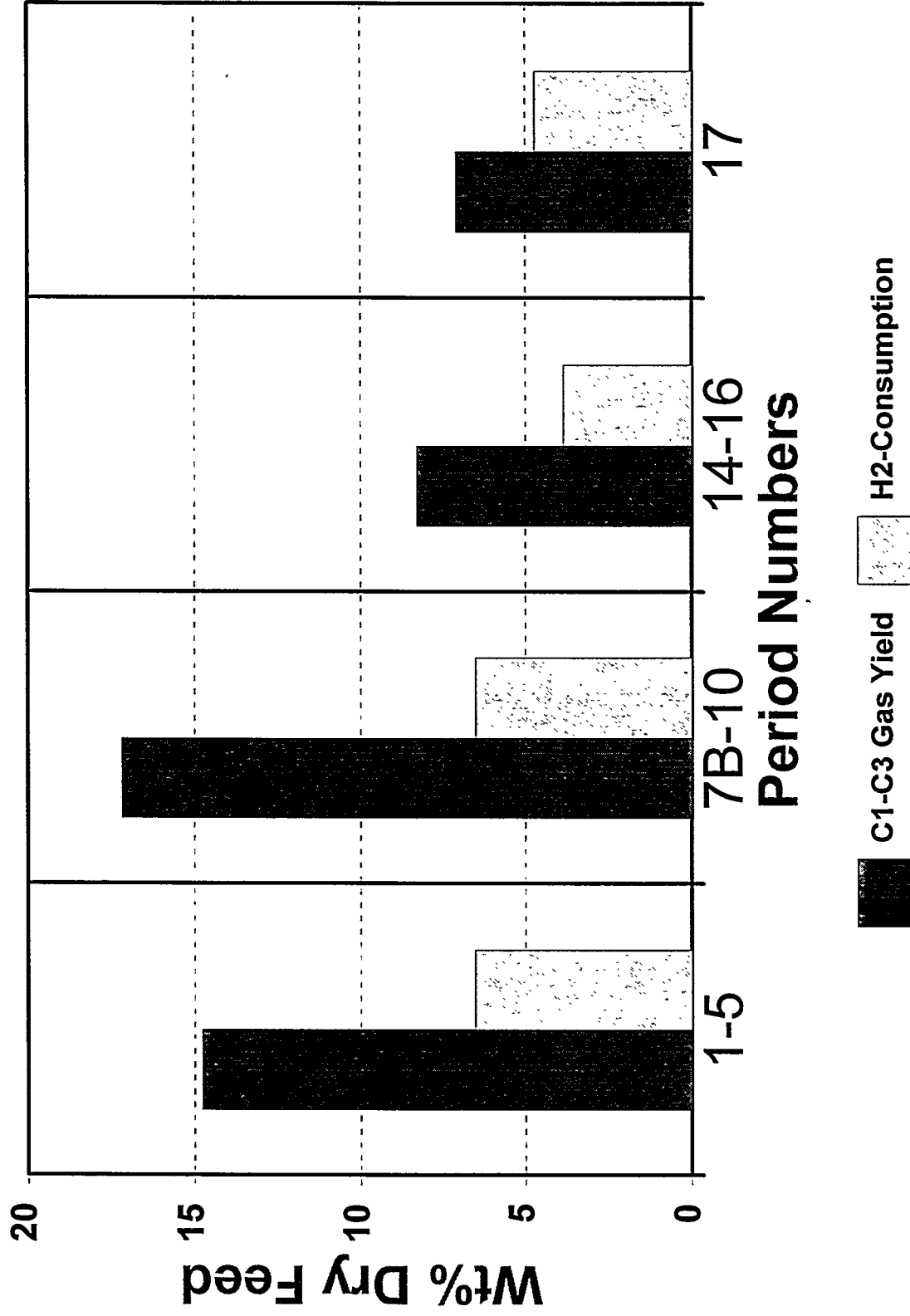


FIGURE 11

CMSL-11: PFL Solubility

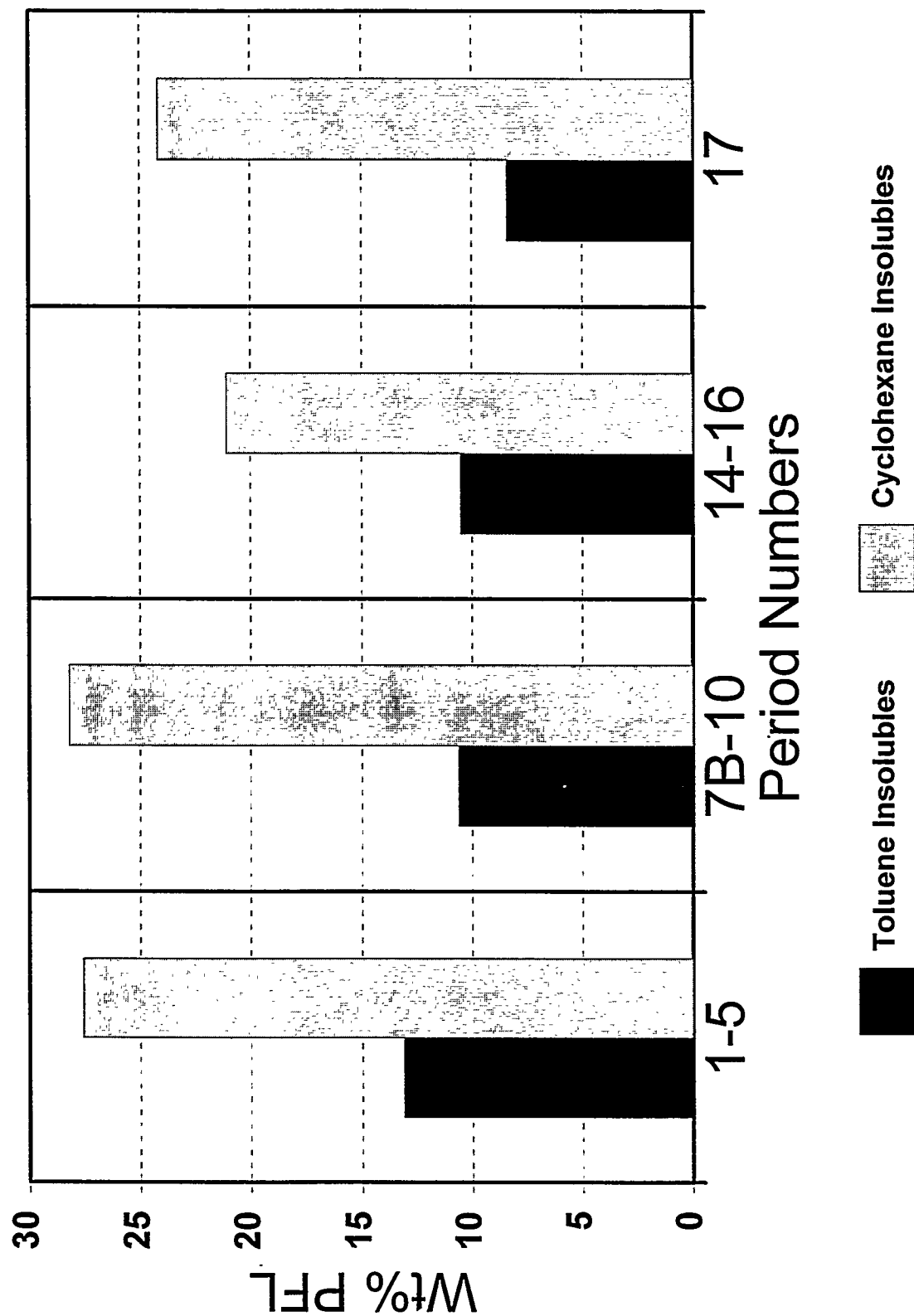
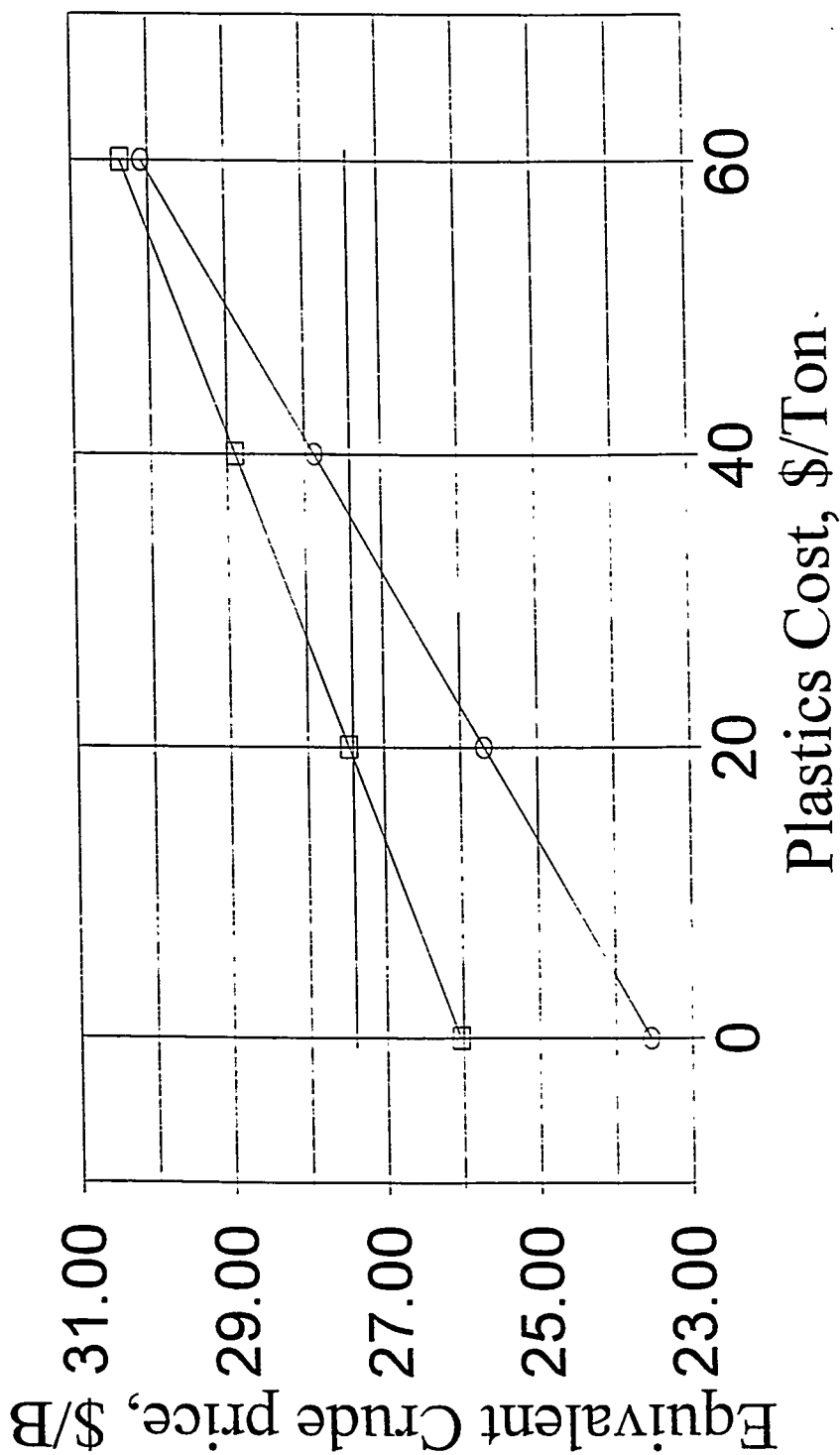


FIGURE 12

Economic Effect of Plastics Cost

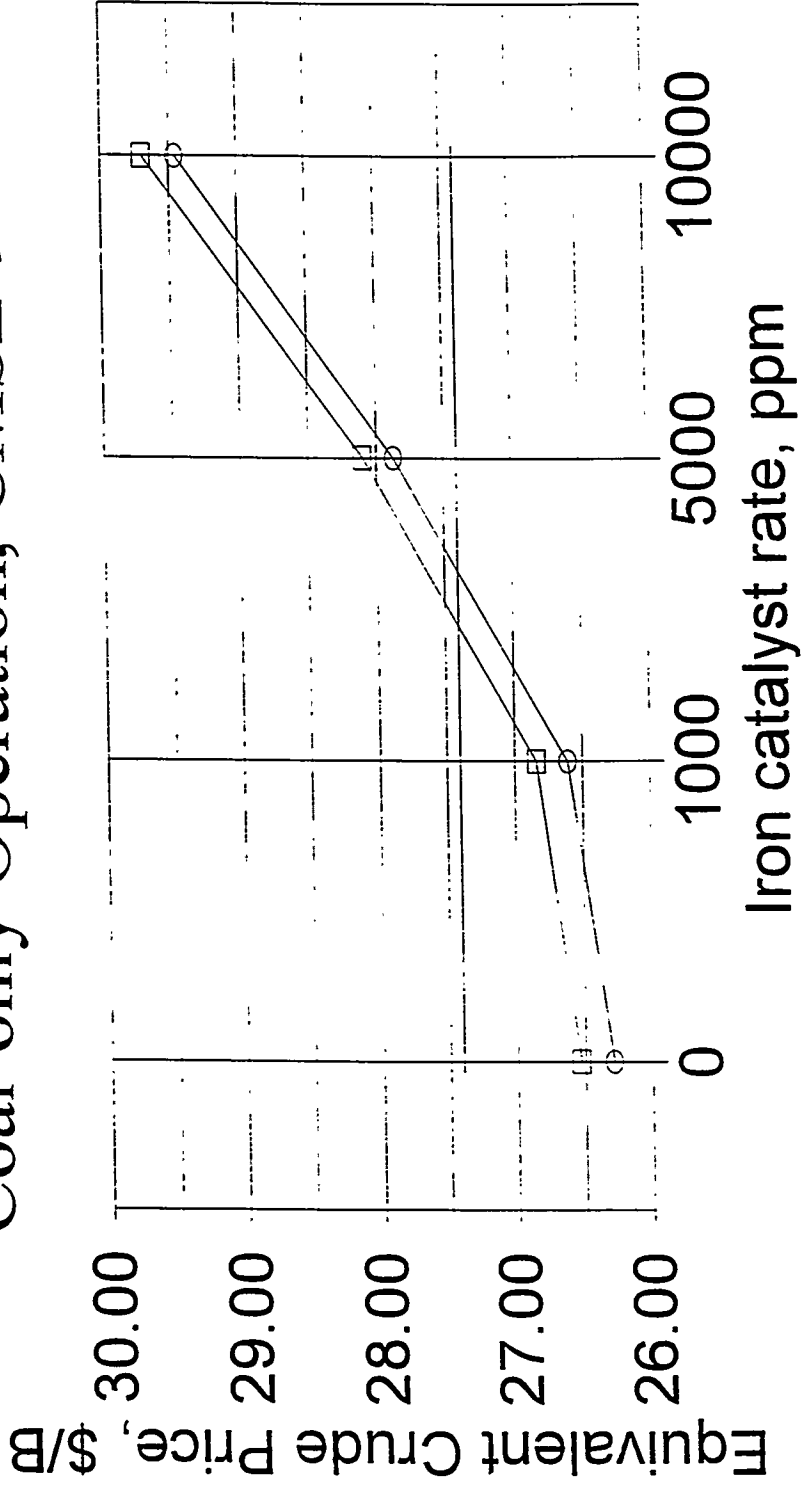
CMSL-9



—□— Per 34 —○— Per 41 —+— Base

FIGURE13

Economic Effect of Iron Catalyst Rate **Coal-only Operation, CMSL-9**



Mo = 300 ppm Mo = 100 ppm Base